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Automation in Determining Solute Concentration and Henry's Constant by Multiple Headspace Extraction Gas Chromatography

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Introduction

The rapid and accurate determination of solute concentration and vapor-liquid phase equilibrium (VLE) partitioning in unknown solutions have significant practical importance in many industrial applications. Headspace gas chromatography (HSGC) was developed to directly analyze the vapor of solutes in a solution. Many HSGC methods have been developed and described in the literature [1-4] and can be used for quantitative and VLE studies. Multiple headspace extraction (MHE) was developed [1, 5] to achieve measurement automation. The MHE procedure is very similar to dynamic gas extraction (or the purge and trap), but is carried out in steps. Therefore, the total peak area extrapolated from the sum of the peak areas measured from each extraction is proportional to the total mass of the solute in the original sample, which is the principle upon which automated quantitative analyses in many industries using MHE GC were based. Kolb and Ettre [1] developed a MHE procedure for determining solute Henry's constant, however, the method was not accurate [6], furthermore, the method has never been carried out experimentally.

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In this study, we present an innovative MHE method and the first experimental study on simultaneous measurements of solute concentration and Henry's constant using a commercial MHE GC system.

Methodology

In a headspace analysis, the total mass of a solute in a sample vial can be expressed as the sum of the solute mass in the liquid and the vapor phases (headspace), i.e., $m = C_G V_G + C_L V_L$. As shown in Fig. 1a, the solute mass vented out of the sample vial through each headspace extraction can be expressed as a certain fraction of the solute vapor in the headspace before venting, i.e., $m_{EX,\,solute} = \varphi \cdot C_G V_G$, where φ is called the sample volumetric flow fraction. Therefore, the total mass of the solute within the vial after the n^{th} headspace extraction can be written as m_n as schematically shown in Fig. 1b,

$$m_n = (C_{Gn} V_G + C_{Ln} V_L) = m_{n-1} - \varphi C_{G(n-1)} V_G = m_1 - \varphi V_G (C_{G1} + C_{G2} + \ldots + C_{G(n-1)})$$
$$= m_1 - \varphi V_G \sum_{1}^{n-1} C_{Gi} \qquad (1)$$

For a solute under infinitive dilution, the vapor-liquid partitioning coefficient is defined $K = C_{L1}/C_{G1} = C_{L2}/C_{G2} = \ldots = C_{Ln}/C_{Gn}$. Therefore, Eqn. (1) can be expressed as:

$$C_{Gn}(V_G + KV_L) = m_1 - \varphi V_G \sum_{1}^{n-1} C_{Gi}\,. \qquad (2)$$

The solute concentration in the headspace after the ith extraction C_{Gi} is proportional to the measured GC peak area A_i, i.e., $A_i = fC_{Gi}$. We can then express Eqn. (2) as a linear equation,

$$\sum_{1}^{n-1} A_i = a + bA_n, \qquad (n = 2, 3, 4, \ldots) \tag{3}$$

where the GC peak areas A_i are measurable quantities, a and b are two constants that can be obtained through linear regression and used to determine the solute concentration C_0 and vapor-liquid partitioning coefficient K:

$$C_0 = \frac{m_1}{V_L} = \frac{a\varphi}{f} \cdot \frac{V_G}{V_L} = \frac{a\varphi}{f}\beta , \tag{4}$$

$$K = -(1 + \varphi b)\beta , \tag{5}$$

where $\beta = V_G / V_L$ is the phase ratio according to Kolb and Ettre [5], f and φ can be obtained through calibration. Detailed derivation of the present method can be found in our previous publication [6].

The solute Henry's constant H is related to K and can be calculated using the following equation,

$$H = \frac{RT}{v^j \cdot K} = -\frac{RT}{v^j(1 + \varphi b)\beta} \tag{6}$$

where H is in pascal, v^j is the molar volume of the solvent in m^3/kmol, R is the universal gas constant (R = 8.315 kJ/kmol/K), T is the solution temperature in Kelvin.

Experimental

Apparatus

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and an HP-6890 capillary gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.)

equipped with an HP ChemStation for data acquisition and analysis. Headspace operating conditions were as follows: compressed air was used for vial pressurization. The pressurization time of the Headspace Sampler: 0.2 min; sample loop fill time: 1.0 min.; and loop equilibration time: 0.05 min. GC conditions: HP-5 capillary column at 30°C; carrier gas helium flow (He): 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flow rates of 35 and 400 mL/min, respectively.

Method Calibration

Both φ and f vary with the headspace operating conditions, mainly the temperature and the headspace volume V_G (or phase ratio β). We established the following procedure for calibration in this study:

1. Prepare a solute (methanol)-water sample solution with known solute concentration (C_0 = 800 mg/L) and solute VLE partitioning coefficient K at a given temperature range.
2. Pipette 50 μL of sample solution into a 20-mL vial, which gives a phase ratio β=399. The phase ratio can be varied as necessary.
3. Put the sample vial into the headspace sampler tray. The headspace GC system is so programmed that it will (1) automatically heat the sample in the vial to a desired temperature (e.g., 40°C) with strong shaking for three minutes to achieve vapor-liquid equilibrium, (2) pressurize the vial by the compressed air, (3) partially withdrawn the vial headspace vapor to fill the sample loop and vent to the atmosphere to return to its initial pressure, (4) the vapor sample is transferred to the GC for analysis and the GC peak area A is recorded.

4. Program the HP Station so that the above procedure is automatically repeated 10 times for multiple headspace extraction analysis.

5. Conduct linear regression analysis using the 10 GC peak areas A_i recorded to obtain the slope b and the intercept a through Eqn (3) with n = 10. Fig. 2 shows the results of a typical regression analysis of the GC peak areas A_i from multiple (10) headspace extractions, where $a = 3461$ and $b = 8.404$.

6. Calculate the calibration constants φ and f from Eqns. (4) and (5) using the literature-given methanol VLE partitioning coefficients [4, 7-11] and known methanol concentration (C_0 = 800mg/L) with the slope b and intercept a obtained, respectively.

7. Repeat procedures (3) to (6), but at a different headspace temperature.

Table I lists the calibration results. We correlated φ and f with temperature T in °C as follows,

$$\varphi(\beta=399) = 0.3777 - 0.00574 \cdot T + 7.7614 \times 10^{-5} \cdot T^2 \qquad (7)$$

$$f(\beta=399) = 437 + 3.1 \cdot T - 0.06 \cdot T^2 \qquad (8)$$

Equations (7) and (8) are valid for any solute-solvent systems under headspace GC conditions used in the present study. The effect of phase ratio β on f can be directly calculated using eqn. (4). The effect of β on φ can be accounted for using the following equation without recalibration [9], assuming that headspace operating conditions (the temperature and the pressurization pressure; therefore, the total volumetric flow into the headspace) remain the same, such as at a sufficiently large phase ratio (β>10),

$$\varphi(\beta) = \frac{\beta_{cal}}{\beta_{cal}+1}\frac{\beta+1}{\beta}\varphi(\beta_{cal}) = \frac{399}{400}\cdot\frac{\beta+1}{\beta}\cdot\varphi(\beta=399) \qquad (9)$$

Results and Discussion

The results presented below were based on our previous study [6].

The Selection of Phase Ratio β

We conducted a mathematical precision analysis of the present MHE GC method [6]. The results indicated that there is an optimum phase ratio β at which the uncertainty is minimum for a given solute-solvent system or a given solute partition coefficient (or Henry's constant). Furthermore, the optimum phase ratio, β_{opt}, correlates very well with the Henry's constant to the following relationship as shown in Fig. 3,

$$\beta_{opt} = K \qquad (10)$$

This relationship agrees with the recommendation of Ioffe and Vitenberg [12] in designing MHE experiments. Fig. 3 also shows the boundaries within which the uncertainties will be less than 10% to avoid difficulties in choosing the optimum β with an unknown *K*.

Solute Concentration Measurement

We conducted comparison measurements of methanol concentrations in nine environmental samples collected from a kraft pulp mill with concentrations ranging from 50 – 1000 mg/L, using both the present MHE method and an indirect HSGC method [2, 3]. As listed in Table II, excellent agreements were obtained between these two methods.

Henry's Constant Measurement

We measured the Henry's constants of isopropanol and ethanol in water solutions at a temperature range of 40-80°C using the present MHE GC method (Eqn. (6)). We compared our measurements to those obtained by Kolb et al. [13] using a direct headspace

GC method. Linear regression shows that the logarithm of the Henry's constants fits very well to the inverse of the temperature in Kelvin, as shown in Fig. 4. Correlation coefficients of 0.9999 and 0.9986 were obtained from the fitting of the isopropanol and ethanol data reported by both Kolb et al. [13] and as measured by the present MHE method. We also plotted ± 10% relative error bars of our data based on our replica measurements, most of the data points fall onto the two fitted lines within the ± 10% error bars.

Conclusion

We achieved measurement automation in simultaneous determination of solute concentration and Henry's constant using a novel multiple headspace extraction GC method. We also provided detailed MHE experimental procedures and conducted first MHE GC experiment study. The measured methanol concentrations in several samples from a kraft pulp mill are in good agreement with those measured by an indirect HSGC method. The measured Henry's constants of isopropanol and ethanol in water solutions are in excellent agreement with those in the literature. The present method is very simple, efficient, and fully automated. It can be easily applied to any environmental and industrial samples with complicated matrices.

Acknowledgment

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References

1. KOLB, B. and ETTRE, L.S., "Static Headspace-Gas Chromatography Theory and Practice," John Wiley & Sons, Inc., New York, 1997.
2. DROZD, J. and NOVAK, J., J. Chromatogr., 136, 37 (1977)
3. CHAI, X.S., DHASMANA, B., and ZHU, J.Y., J. Pulp & Paper Sci., 24(2), 50 (1998).
4. CHAI, X.S. and ZHU, J.Y., J. of Chromatography A, 799, 207 (1998).
5. KOLB, B. and ETTRE, L.S., Chromatographia, 32(11/12), 505 (1991).
6. CHAI, X.S. and ZHU, J.Y., Analytical Chemistry, 70(16), 3481 (1998).
7. HOFSTEE, M.T., KWANTES, A., and RIJNDERS, C.W.A., Symp. Dist. Brighton, 105 (1960).
8. PIVIDAL, K.A., BIRTIGH, A., and SANDLER, S.I., J. Chem. Eng. Data, 37, 484 (1992).
9. DALLAS, A.J., Ph.D. Dissertation, University of Minnesota, Minneapolis, MN, 1993.
10. KOONER, Z.S., PHUTELA, R.C., and FENBY, D.V., Aust. J. Chem., 33, 9 (1980).
11. LEBERT, A., and RICHON, D.J., J. Agric. Food Chem. 32, 1156 (1984).
12. IOFFE, B.V. and VITENBERG, A.G., Chromatographia, 11, 282 (1978).
13. KOLB, B., WELTER, C., and BICHLER, C., Chromatographia, 34, 235 (1992).

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Fig. 1

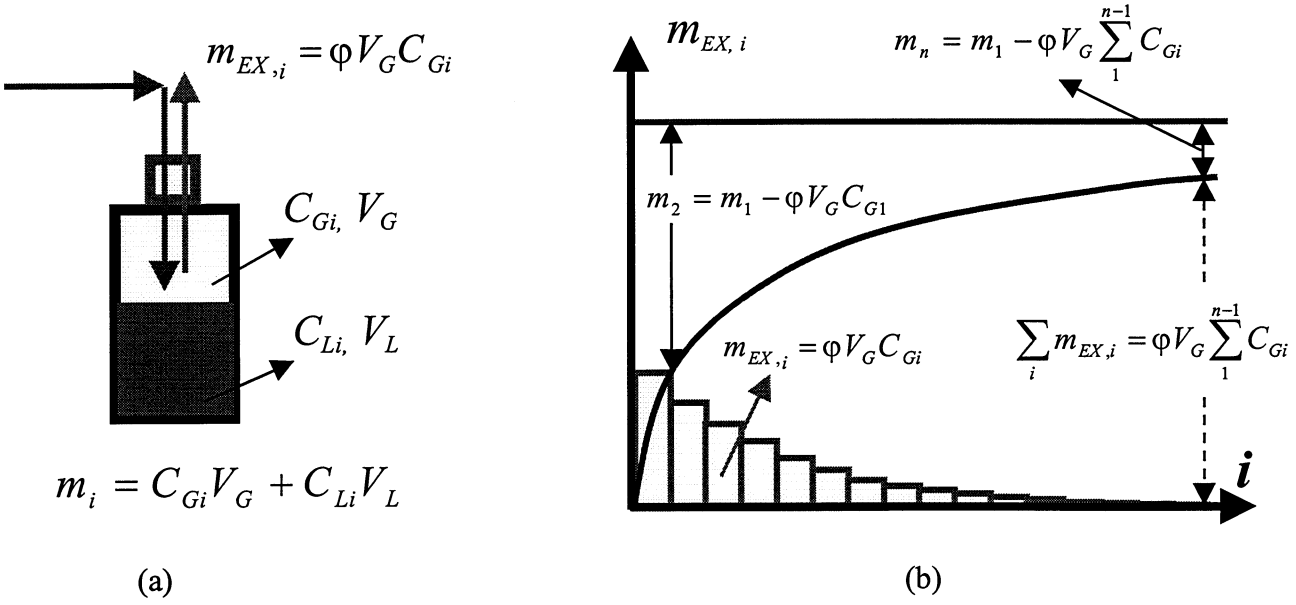
$m_{EX,i} = \varphi V_G C_{Gi}$
$C_{Gi,}\ V_G$
$C_{Li,}\ V_L$
$m_i = C_{Gi}V_G + C_{Li}V_L$
(a)
$m_{EX,\,i}$
$m_n = m_1 - \varphi V_G \sum_1^{n-1} C_{Gi}$
$m_2 = m_1 - \varphi V_G C_{G1}$
$m_{EX,i} = \varphi V_G C_{Gi}$
$\sum_i m_{EX,i} = \varphi V_G \sum_1^{n-1} C_{Gi}$
i
(b)

Fig. 2

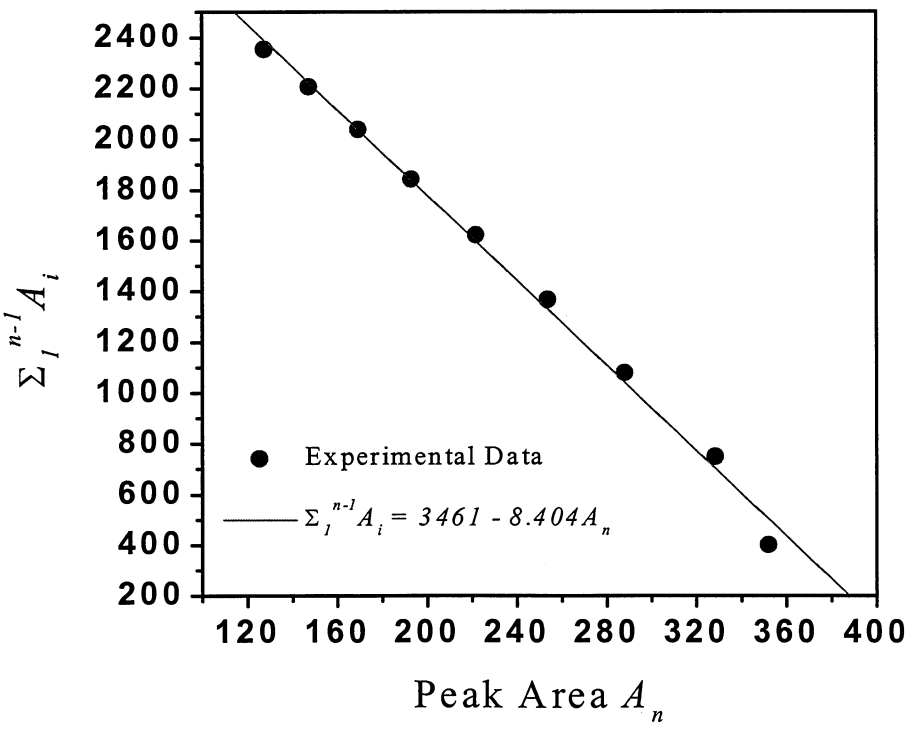
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
120 160 200 240 280 320 360 400
$\Sigma_1^{n-1} A_i$
Peak Area A_n
Experimental Data
$\Sigma_1^{n-1} A_i = 3461 - 8.404 A_n$

Fig. 3

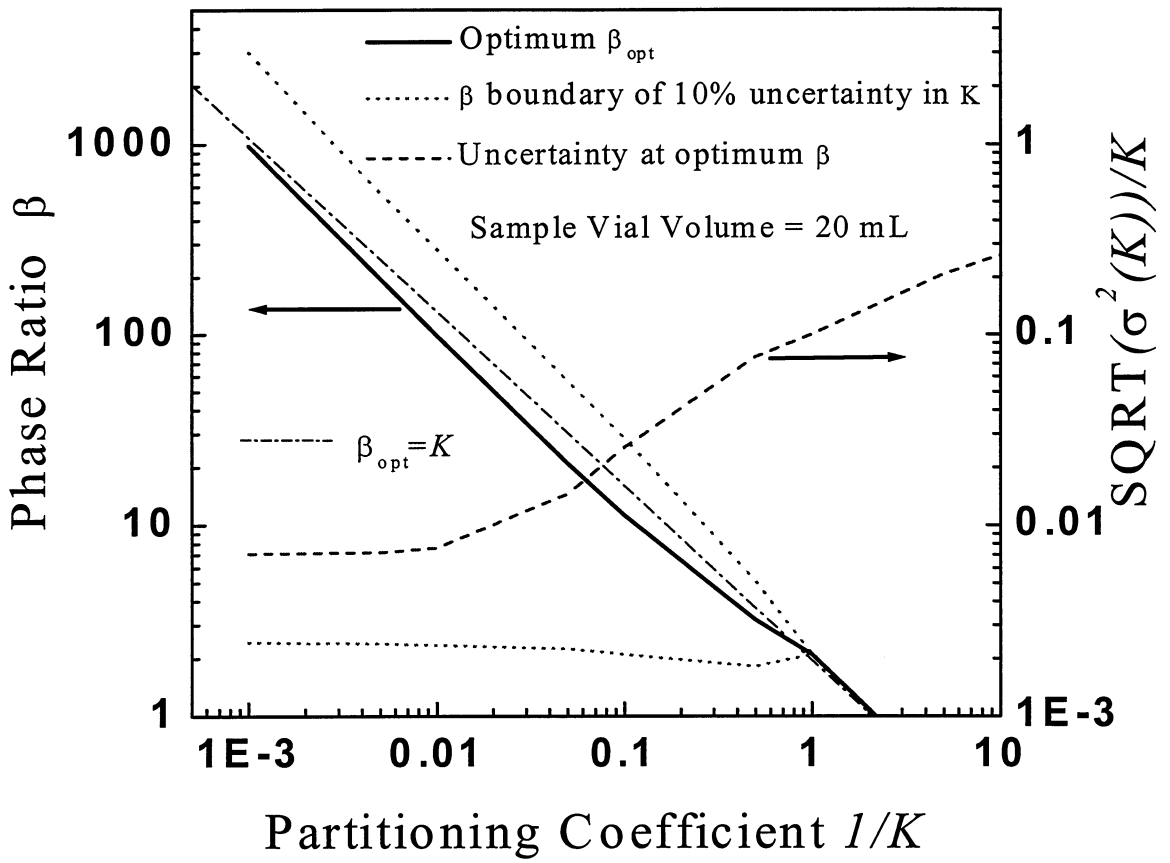
Optimum β_{opt}
β boundary of 10% uncertainty in K
Uncertainty at optimum β
Sample Vial Volume = 20 mL
$\beta_{opt}=K$
Phase Ratio β
1000
100
10
1
1E-3
0.01
0.1
1
10
SQRT($\sigma^2(K)$)/K
1
0.1
0.01
1E-3
Partitioning Coefficient 1/K

Fig. 4

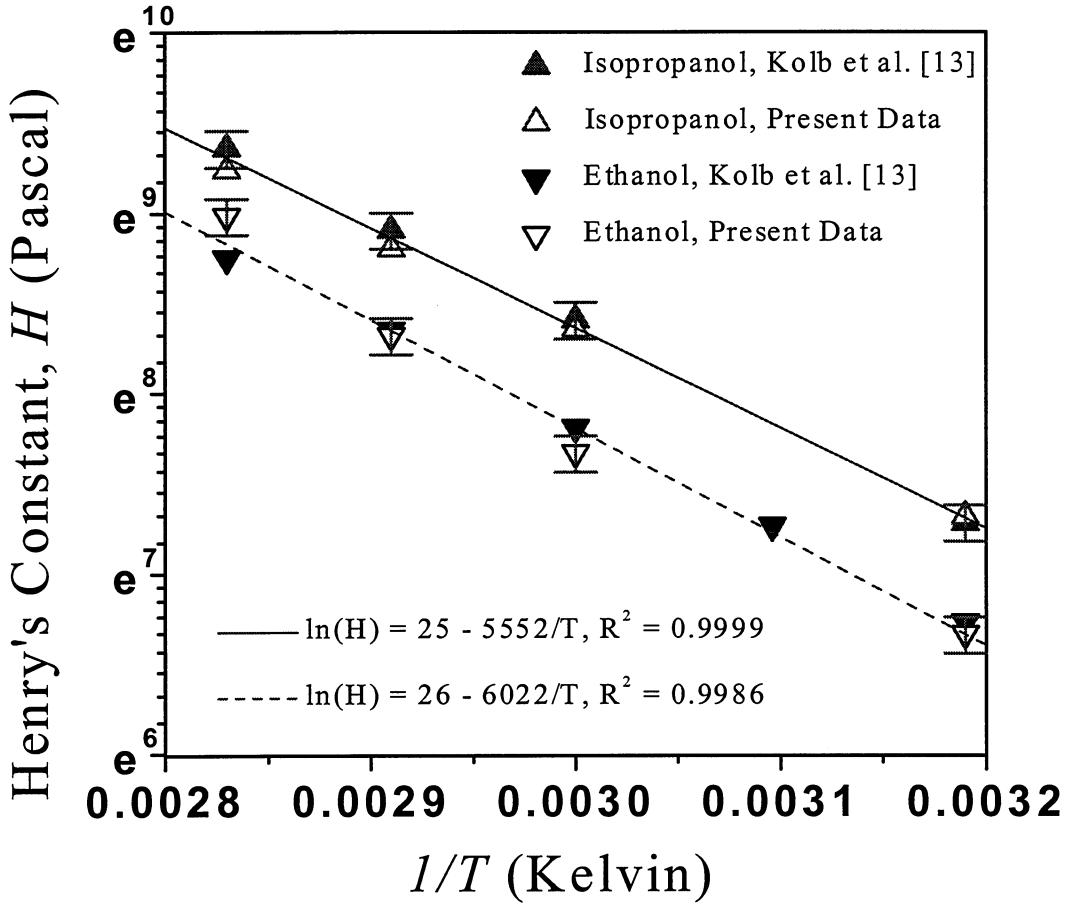
Henry's Constant, H (Pascal)
e10
e9
e8
e7
e6
0.0028
0.0029
0.0030
0.0031
0.0032
1/T (Kelvin)
Isopropanol, Kolb et al. [13]
Isopropanol, Present Data
Ethanol, Kolb et al. [13]
Ethanol, Present Data
ln(H) = 25 - 5552/T, R2 = 0.9999
ln(H) = 26 - 6022/T, R2 = 0.9986

Table I

Temperature (°C)	Partitioning Coefficient K (Literature)	b (Regression Obtained)	φ (Calibrated from Eqn. (5))	a (Regression Obtained)	f (Calibrated from Eqn. (4))
40	0.00044	-23.12 ± 0.41	0.271	3205 ± 36	468
50	0.00071	-14.92 ± 0.12	0.286	2815 ± 14	433
60	0.00112	-9.83 ± 0.13	0.313	2496 ± 15	420
70	0.00170	-6.61 ± 0.12	0.354	1849 ± 18	353
80	0.00260	-4.55 ± 0.06	0.416	1352 ± 10	303
Relative Standard Deviation (RSTD)	N/A	1.4%	N/A	0.8%	N/A

Table II

Sample No.	Methanol Concentration (mg/L)		Relative Difference (%)
	Previous method [2, 3]	Present MHE method	
1	53	52	-1.9
2	94	91	-3.2
3	183	183	0.0
4	311	331	6.4
5	402	390	-2.3
6	613	605	-1.0
7	678	700	3.2
8	775	808	4.3
9	969	992	2.4